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**DEVELOPMENT OF FIXED-NUCLEI
APPROXIMATIONS OF
ELECTRON-MOLECULE SCATTERING AND
THE ADIABATIC THEORY OF
ROTATIONAL EXCITATION**

A. TEMKIN

JUNE 1970



GODDARD SPACE FLIGHT CENTER

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DEVELOPMENT OF THE FIXED-NUCLEI APPROXIMATIONS
OF ELECTRON-MOLECULE SCATTERING AND THE ADIABATIC
THEORY OF ROTATIONAL EXCITATION

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This report is based on an invited talk given by the author to the Washington, D. C.
Meeting of the American Physical Society, April 27, 1970.

DEVELOPMENT OF FIXED-NUCLEI APPROXIMATIONS
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INTRODUCTION

In the first talk of this afternoon's session you heard Dr. Lane present some impressive results of electron scattering from H_2 calculated from a formalism¹ which, particularly when electron exchange is included², naturally fits the description "rotational close coupling."

The significant thing about the calculations of Dr. Lane and his collaborators when they included exchange either semi-phenomenologically³ or directly⁴ together with polarization is that they then contain sufficient dynamics and symmetry to show what this rather complicated formalism is intrinsically capable of.

The intent of this talk is to present a complementary approach to the scattering problem which starts from a somewhat less fundamental point of view, but within its framework can be carried out both more consistently and more rigorously, and as we shall it is capable of very great accuracy. Thus I think I can fairly say that it is destined to replace the rotational close coupling as a method of calculating most aspects of electron-molecule scattering.

FIXED-NUCLEI THEORIES

The basic idea of this approach is supremely simple and for that reason not new. It is to replace the molecule by one in which the nuclei are fixed during the whole scattering process. The classical justification and limitations of this approximation are given in Figure 1. If the electron velocity v is much faster than the velocity of rotation V , then it is reasonable (but not rigorous) to assume that the nuclei are fixed during the scattering process. On the right you see the "very difficult" analysis by which the condition $v \gg V$ can be transformed into an energy $k^2 \gg (m/M)E_{\text{rot}}$. k^2 is the impacting energy of the electron, and you can see what a fantastically low energy the rhs is when you realize that in almost all cases $E_{\text{rot}} \lesssim 0.01 \text{ eV}$ and $m/M < 10^{-3}$. The critical ratio here is the electron to nuclear mass.

We discuss first the papers of Stier⁵ and Fisk⁶ in which the first applications of the fixed nuclei model were carried out. We see (Fig. 2) an ellipsoidal (or prolate spheroidal) coordinate system is introduced at the outset. The potential between the electron and the nuclei is essential separable in λ and μ when you eliminate the $(\lambda^2 - \mu^2)^{-1}$ factor which is common to the kinetic energy as well. The idea of the Stier-Fisk model is to add something resembling the repulsion of the orbital electrons but without disturbing the separability of the nuclear potential. This can be done by introducing only a λ dependent factor as shown. Physically the factor has the effect of distributing the positive charge

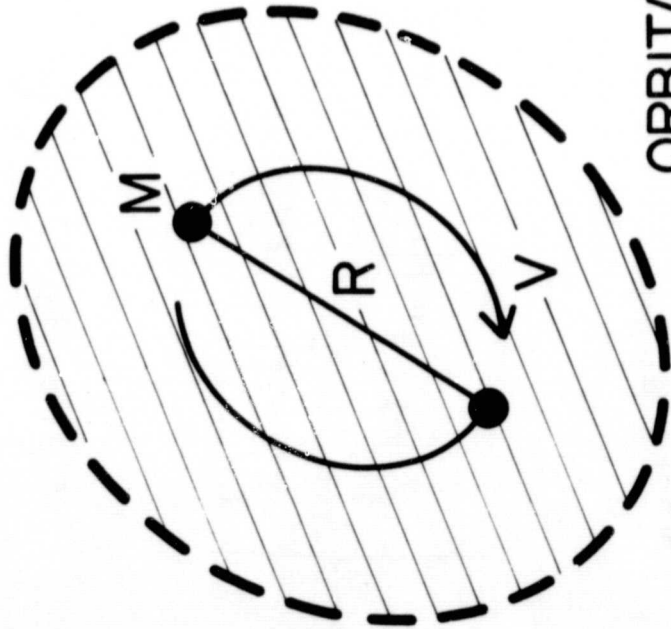
VALIDITY OF FIXED NUCLEI APPROXIMATION



WE DEMAND

$$r \gg V$$

$$r = \sqrt{\frac{2k^2}{m}}$$



ORBITAL ELECTRONS' CHARGE CLOUD

$$V = \omega R$$

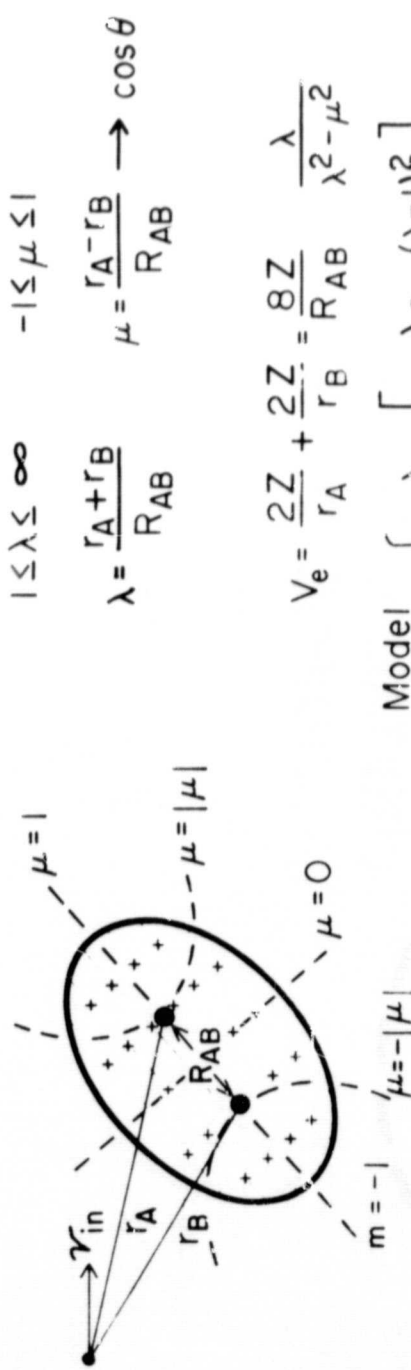
$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

$$I \approx MR^2$$

$$\Rightarrow V \approx \sqrt{\frac{2E_{\text{rot}}}{M}}$$

FINALLY ($r = k$)

$$k^2 \gg \left(\frac{m}{M}\right) E_{\text{rot}}$$



$$1 \leq \lambda \leq \infty \quad -1 \leq \mu \leq 1$$

$$\lambda = \frac{r_A + r_B}{R_{AB}} \quad \mu = \frac{r_A - r_B}{R_{AB}} \rightarrow \cos \theta$$

$$V_e = \frac{2Z}{r_A} + \frac{2Z}{r_B} = \frac{8Z}{R_{AB}} \frac{\lambda}{\lambda^2 - \mu^2}$$

$$\text{Model } V = \begin{cases} \frac{\lambda}{\lambda^2 - \mu^2} \left[1 - \frac{\lambda_0}{\lambda} \frac{(\lambda - 1)^2}{(\lambda_0 - 1)^2} \right] & \lambda < \lambda_0 \\ 0 & \lambda > \lambda_0 \end{cases}$$

$$\bar{\Psi} = \begin{cases} \sum_{\ell, m} A_{\ell, m} e^{im\phi} \left[(1 - \mu^2)(\lambda^2 - 1) \right]^{\frac{m}{2}} S_{m\ell}(R_{AB}; \mu) e^{-\Lambda(\lambda-1)} f(\lambda) & \lambda < \lambda_0 \\ \sum_{\ell, m} e^{im\phi} \left[(1 - \mu^2)(\lambda^2 - 1) \right]^{\frac{m}{2}} S_{m\ell}(R_{AB}; \mu) \left[C_{m\ell} R_{m\ell}^{(1)}(\lambda) + D_{m\ell} R_{m\ell}^{(2)}(\lambda) \right] & \lambda > \lambda_0 \end{cases}$$

$$f(\mu, \phi; \beta_0, \lambda_0) = \frac{1}{k} \sum_{\ell, m} e^{im\eta_{\ell m}} \sin \eta_{\ell m} S_{m\ell}(R_{AB}, \cos \beta_0) S_{m\ell}(R_{AB}, \cos \theta) \cos [m(\phi - \gamma_0)]$$

$$\tan \eta_{\ell m} = (-1)^m \left[\frac{R_{m\ell}^{(1)}(\lambda_0) - (f'(\lambda_0)/f(\lambda_0)) R_{m\ell}^{(1)}(\lambda_0)}{(f'(\lambda_0)/f(\lambda_0)) R_{m\ell}^{(2)}(\lambda_0) - R_{m\ell}^{(2)}(\lambda_0)} \right]$$

Figure 2

throughout the volume of the ellipsoid and reducing the potential outside to zero. By implication then the model puts a layer of negative charge on the surface in order that the potential be zero outside. You see then that the model is pretty crude compared to a real molecule, not to mention the fact that exchange of the scattered and orbital electrons is not at all included. But there is at least one free parameter, λ_0 the boundary ellipsoid by which one can hope phenomenologically to make up for this and I think the effective charge Z was also adjusted to fit some atomic data. That in this spirit the program does succeed is indicated in the next Figure (3). The experimental results of Ramsaner and Kollath⁷ and Golden, Bandel, and Salerno⁸ can be nicely accommodated below 5 eV by Fisk's fit; above his result is definitely low, but I would like to call to your attention the low energy side where his results are definitely too high and going in the wrong direction. For those of you familiar with low energy electron atom scattering, you know that that is a symptom of not including exchange in the calculation. This is about how far this approach takes us but I would like to point out that the backbone of at least Fisk's work — the beautiful spheroidal expansion⁹ and the separable potential will be recognized as the hallmark of Fisk's thesis advisor, Professor Philip M. Morse.

Although the profound effect of exchange in electron-atom scattering had been shown by Morse and Allis¹⁰ in 1933, it took over twenty years beyond Fisk's calculation to show that essentially the same phenomenon operates in electron-molecule scattering also. The calculation was performed by Massey and Ridley,¹¹

Figure 4.

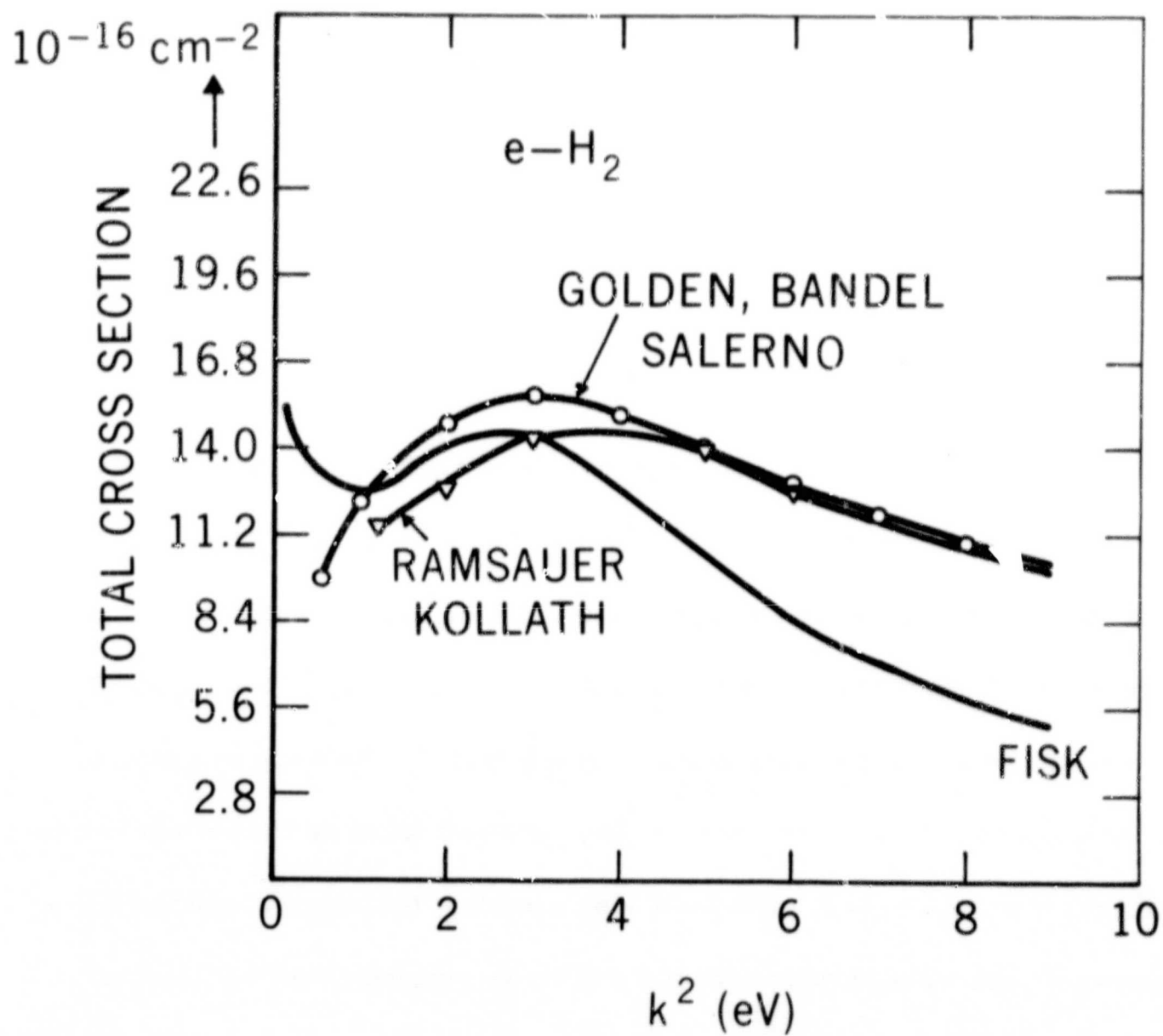


Figure 3

They constructed a totally antisymmetric function for the $e-H_2$ system using spheroidal coordinates for each electron; α and β are the two-component up-down spinors. The scattered orbital F was taken to be of the form given.

The ground state (Σ_g^+) of the H_2 wave function was a separable spheroidal function calculated by Coulson¹². The remaining parameters a , b , and γ are determined by the variational principle — both Kohn and Hulthen were employed. The functional L can be divided into a direct and exchange term. If you retain only L_D , then the resultant "S-wave" phase shift is such as to give you a huge low energy cross section, reminiscent of the Fisk result and in gross disagreement with the experiment. However if you include L_E also, then the cross section is lowered dramatically. Thus for the first time one can say that a fundamental quantitative calculation is in semi-quantitative agreement with experiment. In detail the effect comes from the zero-energy phase shift approaching π rather than zero radians and, in complete analogy with e-atom scattering, it produces a much smaller cross section near the elastic threshold. Finally note that the exchange cross section is larger and increasing more slowly than the experimental results. This is a well known defect of the exchange approximation in e-atom scattering, and to correct for it you must include induced polarization effects; but we will come to that.

With the calculation of Massey and Ridley we have entered the right arena for quantitative calculation. The first step in improving the accuracy is to include higher partial waves. To do this in spheroidal coordinates while at the

MASSEY & RIDLEY PPS A69, 659 (1956)

USE TOTALLY ANTISYMMETRIC WAVE FUNCTION

$$\bar{\Psi} = \frac{1}{\sqrt{6}} \sum_{\text{cyclic permutations of } i, j, k} F(\mathbf{r}_i) \Psi(\mathbf{r}_j, \mathbf{r}_k) \alpha_i (\alpha_j \beta_k - \alpha_k \beta_j)$$

CALCULATE "S-WAVE" SCATTERING $(c = 1/2 \times k \times R_{AB})$

$$F(\mathbf{r}_i) = \frac{1}{\sqrt{1+a^2}} \frac{1}{c(\lambda_i-1)} \left[\sin c(\lambda_i-1) \left\{ a + b e^{-\gamma(\lambda_i-1)} \right\} \left\{ 1 - e^{-\gamma(\lambda_i-1)} \right\} \cos c(\lambda_i-1) \right] \rightarrow \frac{\sin C\lambda_i + \eta_{00}}{C\lambda_i}$$

$$\Psi(j, k) = \phi(j) \phi(k) ; \eta_{00} = \tan^{-1} a - c$$

$$\phi(j) = N e^{-\lambda_j} (1 + f \mu_j^2 + g \lambda_j)$$

FORM L & USE KOHN & HULTHEN v.p.

$$L = \int \Psi (H-E) \Psi = L_D + L_E$$

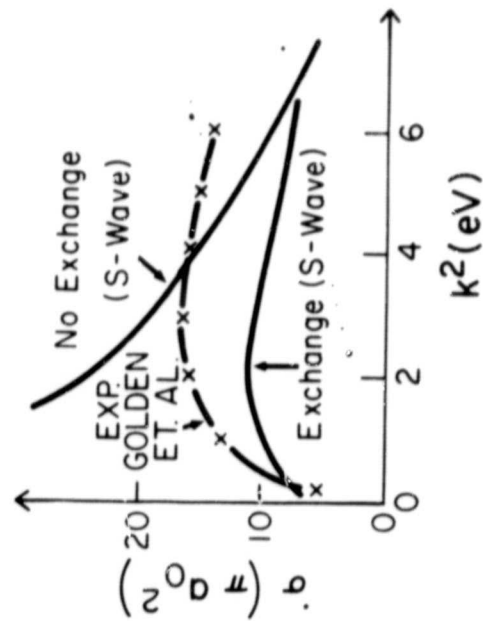


Figure 4

same time retaining the electron-electron interaction as did Massey and Ridley, one must go beyond the separable spheroidal analysis of Stier and Fisk. This was in fact done first by Nagahara¹³ in 1953, but his calculations¹⁴ (1954) for e-H₂ scattering did not include exchange and any agreement his results may contain with experiment are now generally considered to be coincidental. The nonseparable spheroidal analysis has more recently been repeated by Takayanagi¹⁵ and by Hara¹⁶. The latter has gone much further in that he has actually done the calculation including polarization as well as exchange.

Before discussing his results let us note that a spheroidal analysis carries with it the following disadvantages. The spheroidal harmonics in terms of which the scattering amplitude is expressed¹⁷,

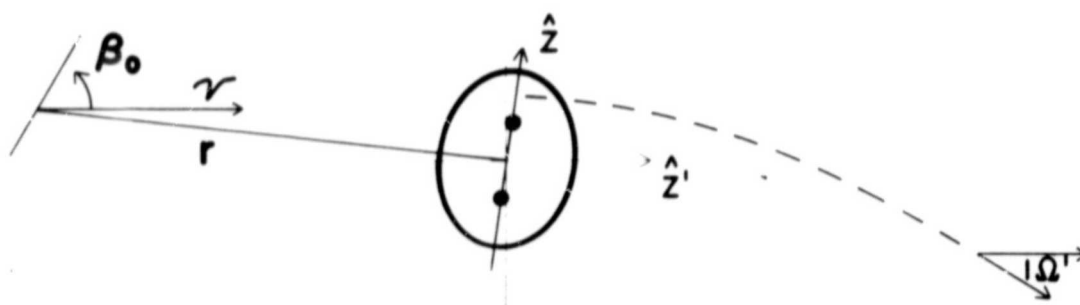
$$S_{m\ell}(R_{AB}, \cos \beta_0) = \sum_{s=m}^{\infty} d_{\ell,s}(R_{AB}) P_{\ell,m+s}(\beta_0)$$

are seen to depend on the internuclear distance, R_{AB} , of the particular molecule being investigated. This means that the experimentalist would have to infer different scattering parameters for different molecules (having presumably different R_{AB} 's) even though their observed scattering rates were the same. Not only is this inconvenient but it is really unphysical, because the internuclear separation is something which isn't observed in the scattering experiment at all. If we made the analysis in terms of $P_{\ell,s}(\beta_0)$ then this problem would not even arise.

In the next Figure (5) we therefore consider the analysis of electron molecule scattering in spherical harmonics. The references given at the top of that figure are given more completely in the list of references^{18, 19}. The most salient observation is really quite obvious if you think about it: considering the internuclear axis as fixed, then the Hamiltonian is independent of the direction of the incoming beam. Secondly if the amplitude is to be invariant with respect to joint rotations of the incoming direction and the internuclear axis, that is to say if you rotate the direction of the incoming beam you change by definition the lab-fixed frame and if simultaneously you rotate the internuclear axis by the same amount, then it is clear that you change nothing at all in the "new" laboratory system of coordinates. Under these circumstances the scattering amplitude must have the form shown, but in addition the $f_{\ell_i \ell_j m}(\beta_0)$ must factor according to the second equation. Now that is the essential item: the D functions are the rotational harmonics — the well known matrix elements of the rotation group; they are known functions of β_0 . On the other hand the scattering parameters $a_{\ell_i \ell_j m}$ are the only numbers which are determined by the dynamical equations and they are independent of β_0 . Thus the dynamical problem can be solved once and for all and the dependence on β_0 simply multiplies those numbers as a factor. In addition to its simplicity, this will be seen to have important implication for the adiabatic theory of rotational excitation. Furthermore in the uncoupled approximation, which turns out in many cases to be an excellent one, the $a_{\ell_i \ell_j m}$ reduce to a very familiar form involving phase

ELECTRON-DIATOMIC MOLECULAR SCATTERING IN SPHERICAL COORDINATES

TEMKIN & VASAVADA } P.R. { $\frac{160}{186}$, 109 (1967)
 TEMKIN & VASAVADA, CHANG, SILVER }



OBSERVATIONS

1. HAMILTONIAN IN INTERNUCLEAR FRAME IS INDEPENDENT OF THE INCIDENT DIRECTION OF SCATTERED ELECTRON (β_0)
2. THEREFORE YOU CAN "FACTOR" THE SCATTERED AMPLITUDE :

$$f(\beta_0, \Omega') = \sum_m \sum_{l_i l_j} f_{l_i l_j m}(\beta_0) Y_{l_i m}(\Omega')$$

WHERE

$$f_{l_i l_j m}(\beta_0) = \sum_m a_{l_i l_j m} D_{m' m}^{(l_i)}(\beta_0) D_{0 m}^{(l_j)*}(\beta_0)$$

- (a) FACTORING MEANS $a_{l_i l_j m}$ ARE INDEPENDENT OF β_0
- (b) $a_{l_i l_j m}$ ARE COUPLED IN $l_i - l_j$ BECAUSE OF ABSENCE OF SPHERICAL SYMMETRY OF H BUT UNCOUPLED IN m BECAUSE OF CYLINDRICAL SYMMETRY (ABOUT \hat{z}). ALSO BY PARITY CONSERVATION $(-1)^{l_i} = (-1)^{l_j}$
- (c) IN UNCOUPLED APPROXIMATION

$$a_{l_i l_j m} \rightarrow \delta_{l_i l_j} \delta_{l_i l_j} \frac{\sqrt{4\pi(2l+1)}}{k} e^{i\eta_{l m}} \sin \eta_{l m}$$

- (d) THE OPTICAL THEOREM IS SATISFIED FOR ALL β_0 :

$$\sigma(\beta_0) = (4\pi/k) \text{Im } f(\beta_0, 0)$$

Figure 5

shifts $\eta_{\ell m}$. Here it is quite obvious what price we have paid for eliminating β_0 from the dynamical problem — the $\eta_{\ell m}$ depend on the magnetic quantum member m as well as ℓ . Generally this is a small price to pay as we shall see when we look at some radial equations. And finally the optical theorem holds for all angles of orientation β_0 depending only on the dynamical approximations which determine the $a_{\ell_i \ell_j m}$ — the specific conditions are given in our second paper¹⁹.

In summary, then we can say that the partial wave expansion can be consistently carried out and it is complete in principle. In practice, however, all things must be truncated, and we must still inquire as to dynamical justification of a spherical treatment. In Figure 6 we consider that problem. The general justification is that given in item (1) with item (2) having just been discussed. If indeed these two items suffice, then we may use all the analogous methods used in scattering from atomic systems. But with regard to the question of the dynamical justification of a spherical expansion none of these three items really proves its accuracy. For as indicated in item 4 if the electron is accelerated into the target, its wave length in the interior will be effectively shorter and it may probe the singularities with the nuclei. They are pictured as the solid curves on the right hand part of the figure (6). If one makes a single center expansion of the nuclear potentials, then the lowest order term V_0 is indeed a crude approximation in the vicinity of $\pm 1/2 R_{AB}$. The dynamical advantages, then, of a spheroidal coordinate is not that it simplifies the partial wave analysis,

JUSTIFICATION OF SINGLE CENTER EXPANSION



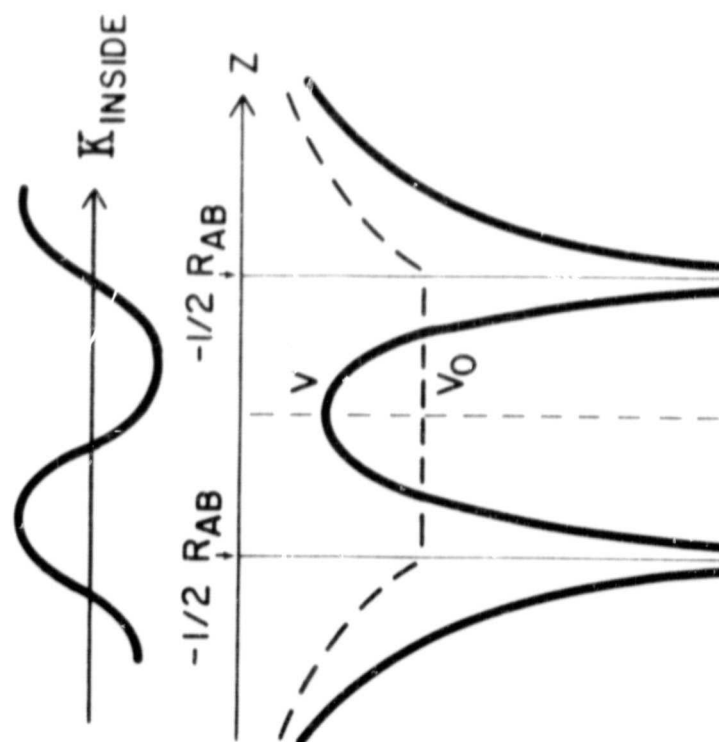
JUSTIFICATION

1. IF $\frac{1}{k} \equiv \lambda \gg R_{AB}$ THEN ELECTRON SHOULD NOT BE ABLE TO PROBE MOLECULAR CORE.
 2. PARTIAL WAVE EXPANSION CAN BE CONSISTENTLY CARRIED OUT.
 3. EXPLOIT ANALOGIES WITH E-ATOM SCATT. METHODS.
- ### QUESTIONS
4. IF ATTRACTIVE SINGULARITIES WITH NUCLEI ARE STRONG ENOUGH,

$$\text{THEN } \frac{1}{K_{\text{INSIDE}}} \equiv \Lambda_{\text{INSIDE}}^{(?) \approx R_{AB} \text{ EVEN}}$$

IF (2.) IS SATISFIED.

5. IF ONE USES ELLIPSOIDAL COORDINATES, THEN THESE SINGULARITIES CAN BE TREATED EXACTLY. THAT IS THE REAL ADVANTAGE OF SUCH COORDINATES. PARTIAL WAVE EXPANSION IS JUST AS COMPLICATED AS IS SPHERICAL COORDINATES.



EXPAND NUCLEI POTENTIALS

$$-\frac{2}{r_A} - \frac{2}{r_B} = \sum_{n=0}^{\infty} V_n(r) P_n(\cos \theta)$$

AND TARGET WAVE FUNCTION

$$\Phi_M^{(N)}(r_2) = \sum_{n=0}^N \phi_n^{(N)}(r_2) \frac{P_n(\cos \theta_2)}{r_2}$$

Figure 6. The double prime on the summation indices represents even values of n only.

it does not, but rather that it allows these singularities to be included in a natural wave. Note also items on lower right of the slide.

This is about all we can say about this point now. Any further statements about the proof of this pudding will have to come in the eating.

I should, for historical reasons, mention the 1958 single center calculation of Carter, March of Vincent²⁰. It was an extremely crude one, and exchange was only taken into account in an approximate way. Nevertheless it was the first, and it supported the conclusion of Massey and Ridley¹¹ that exchange was essential for lowering the low energy cross section. My unhappiness with that paper comes from the fact that it is one that says the phase shifts would depend on the internuclear axis angle — a misconception which caused Vasavada and me a lot of anguish until we could show how to include it correctly¹⁸.

In the Figure 7 we display in abbreviated form the radial equations for $e\text{-H}_2^1$ scatt. in the uncoupled approximation¹⁸. The wave function from which they are derived is given at the top. $\phi_0^{(N)}$ is the spherically expanded unperturbed target (σ_g) wave function given in Figure 6. In addition the wave function contains a polarization part which will be recognized as just what arises in the method of polarized orbitals²². The philosophy of including the first order distortion ($N = 2$ term) in $\phi_2^{(N)}$ in addition to $\phi_0^{(2)}$ is essentially just the same as including $\phi^{(p01)}$. In the latter case the basic assumption is that the polarizability is not too large and in the former the basic assumption is that the internuclear distance not be too large. In both cases one can not give an

RADIAL EQS. FOR e-H₂⁺ SCATT.

$$\Psi_{lm}^{(N)} = \frac{u_{lm}(r_1)}{r_1} Y_{lm}(\Omega_1) [\Phi_0^{(N)}(r_2) + \Phi_0^{(POL)}(r_1; r_2)] \pm (l \leftrightarrow 2)$$

$$\Phi_0^{(POL)}(r_1; r_2) = \frac{-\epsilon(r_1, r_2)}{r_1^2} \frac{\phi_0^{(POL)}(r_2)}{r_2} \frac{\cos \theta_{12}}{\sqrt{4\pi}}$$

$$\left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + V_0(r) - \delta_{ll} \frac{(3m^2-2)}{5} V_2 - 2 \int_0^\infty \frac{r_{<}^0}{r_{>}} [\phi_0^{(N)}(r_2)]^2 dr_2 \right. \\ \left. + \frac{2\delta_{ll} \delta_{N2}}{\sqrt{5}} \left(\frac{3m^2-2}{5} \right) \int_0^\infty \frac{r_{<}}{r_{>}} \phi_0^{(2)} \phi_2^{(2)} dr_2 \right\} u_{lm}(r) \pm (\text{EXCHANGE TERMS})$$

$$= -\frac{2}{3} \frac{u_{lm}(r)}{r^4} \int_0^r r_2 \phi_0^{(N)} \phi_0^{(POL)} dr_2 \pm \left(\begin{matrix} \text{EXCHANGE} \\ \text{POLARIZATION TERMS} \end{matrix} \right)$$

WHERE

$$V_l(r) = \begin{cases} 4r^l / \left(\frac{1}{2}R_{AB}\right)^{l+1} & r < \frac{1}{2}R_{AB} \\ 4\left(\frac{1}{2}R_{AB}\right)^l / r & r > \frac{1}{2}R_{AB} \end{cases}$$

Figure 7

a priori limit as to what too large means but in practice it appears that one can be pretty liberal, at least for the lightest nuclei.

The radial equations are seen to be quite similar to what one gets in e-hydrogen atom scattering²². On the rhs we see a direct polarizability term. The exchange and exchange polarization terms are those multiplied by \pm ; they represent the difference between singlet and triplet scattering equations.

When we come to p-waves ($\ell=1$) we see the first manifestation of the m dependence of the equations. In particular the V_2 term is seen to go like r^{-3} at infinity — that is the quadrupole term, and it changes sign from attractive for $m = 0$ to repulsive for $|m| = 1$. To some extent these effects are opposed by the first order correction; but since $|\phi_2^{(2)}| \ll |\phi_0^{(2)}|$ the magnitude of this modification are indeed small.

All these effects are discernible in the numerical results¹⁸ some of which are graphed on the next Figure (8). On the left we see in the 'S phase shifts trial effect of polarization; which is always attractive, is to increase them algebraically. Also we see that first order (nonspherical) effects are very small. For comparison we have plotted the 1S e-He⁺ phase shifts calculated by Sloan²³ at the top. You can readily see that He⁺ in the single-center target that H₂⁺ would become if its nuclei were to come together. In that case, however, the spherical treatment takes full account of the singularity of the nuclear potential and one sees the vast increase of the phase shift. This gives one some concern as to the quantitative accuracy of the single center expansion.

$e\text{-H}_2^+$ PHASE SHIFTS

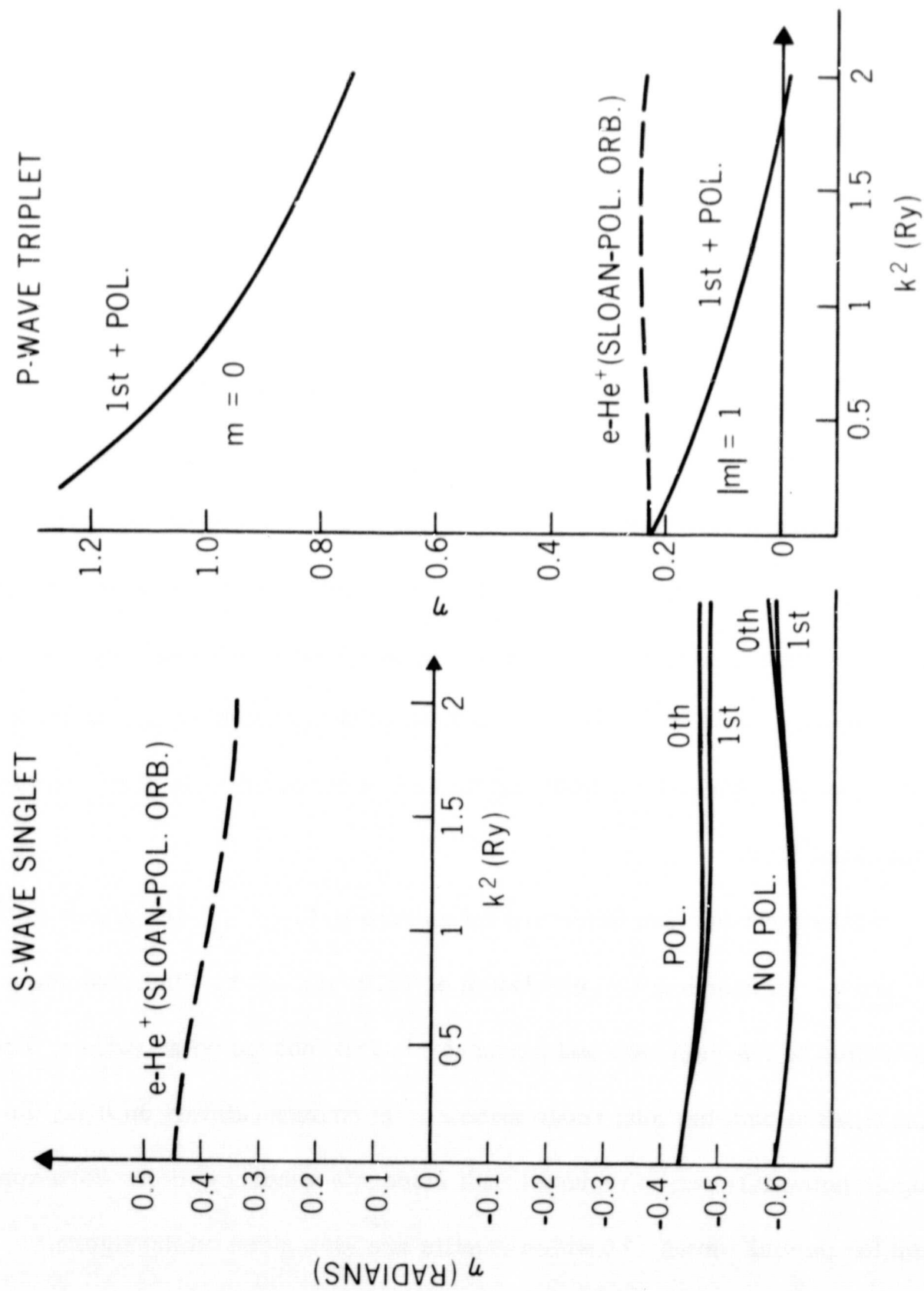


Figure 8

There is some consolation in the fact that the first order correction actually reduces the phase shifts slightly as you see. Nevertheless I think there is only one way to test the accuracy of the single-center calculation quantitatively and that is to do the calculation in spheroidal coordinates. Such a calculation is being done at our laboratory by Dr. A. B. Ritchie.

On the right you see some 3P phase shifts. First notice how the attractive quadrupole potential in the $m = 0$ case increases that phase shift over the repulsive $|m| = 1$ quadrupole potential. Secondly note how large the $^3P_{m=0}$ phase shift is! It actually goes to about 80° at zero energy and it really has no counterpart even in the atomic case ($e\text{-He}^+$). But it also can not simply be described as a pure quadrupole effect. It was this circumstance which led to our suggestion¹⁸ that it was the counterpart of such an enhancement which might account for the Σ_u compound state of the H_2^- . This so-called "resonance" was most vividly found experimentally by Schulz and Asundi in the production of H^- ions in $e\text{-}H_2$ collisions²⁴.

Without further ado therefore let us turn to the Σ_u , $e\text{-}H_2$ phase shifts, Figure 9. In essence the calculation of Tully and Berry²⁵ includes the permanent distortion of the molecule and exchange, but no induced polarization. The induced polarization plus the long range effects of permanent distortion (i.e., the quadrupole potential) can be included with moderate accuracy in the Born approximation for partial waves $\ell > 0$ which results are also given on the figure.

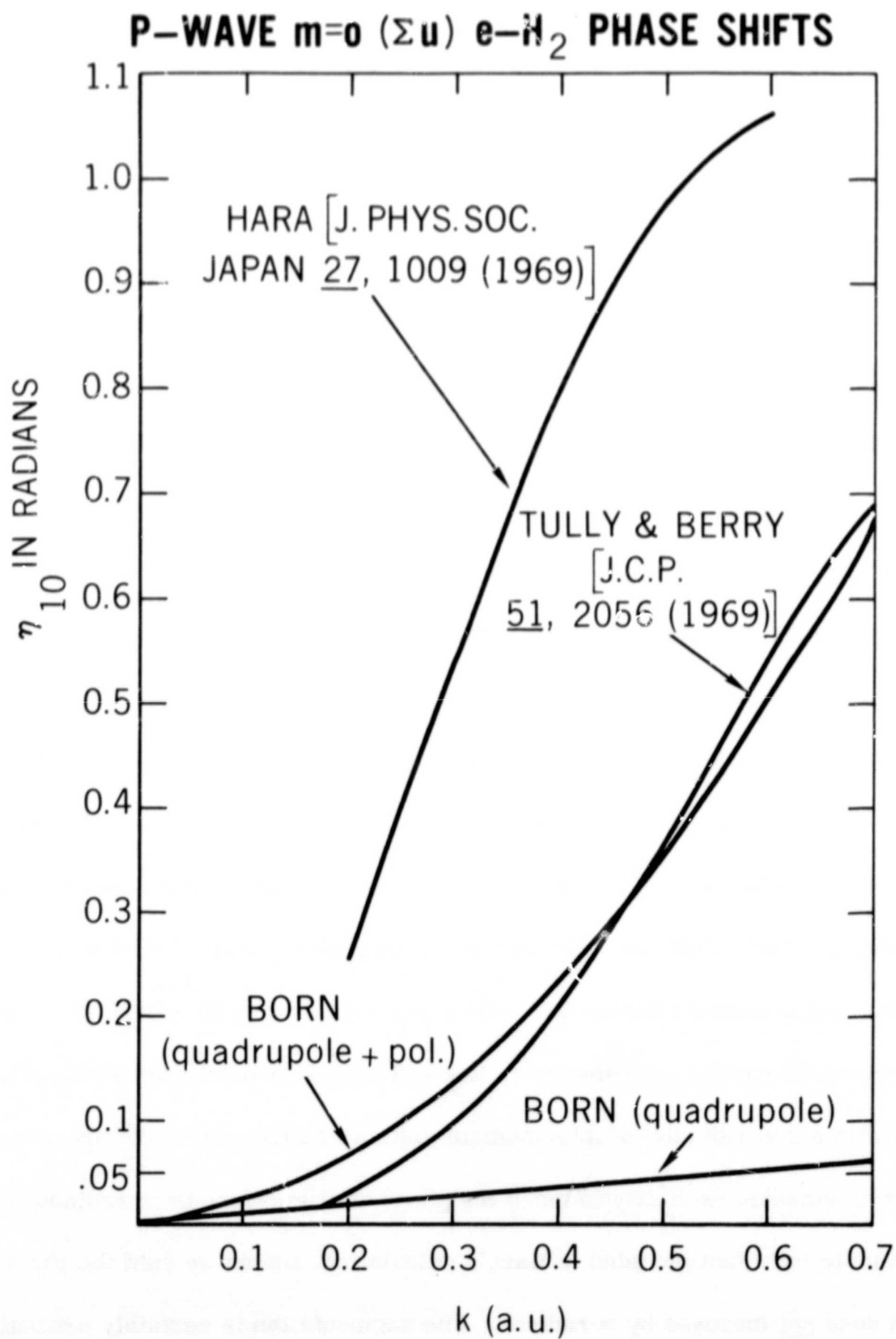


Figure 9

If you add the polarization contribution to Tully and Berry you get something very close to Hara's results¹⁶. Hara has made the most complete calculation of electron- H_2 scattering thus far. In addition to including permanent distortion automatically by using spheroidal coordinates, he has also added polarization²⁶. The only objection one might take to this important calculation is that it does not include the exchange polarization terms that would arise in a complete polarized orbital calculation²². Now looking at Hara's \sum_u results, we do indeed see the very pronounced enhancement of that partial which really does accord with the similar enhancement that Vasavada and I found in $e-H_2^+$ scattering¹⁸. The inferred cross sections from these scattering parameters agree with the experimental results very well. We shall see one example later on. Nevertheless you see that even Hara's phase shift do not pass through $\pi/2$ radians; thus to the extent that a resonance has been discussed (I mention in particular Bardsley, Herzenberg, and Mandl)²⁷ in this partial wave, the term must be taken loosely. The reason I don't like the word is because resonance implies various things about the shape and maximum values that various partial cross sections should have which don't really accord accurately with experimental results. Furthermore theoretically a resonance is usually associated with a specific kind of intermediate state which dominates the process and must be included explicitly to make the phase shift increase by π radians. No such state is in fact included in Hara's calculation, and as we said the phase shift does not increase by π radians. The augmentation is certainly present,

but I would recommend the word "enhancement" for it. I even think the term "shape resonance" is either too strong or too ambiguous.

ADIABATIC THEORY OF ROTATIONAL EXCITATION

We now turn to the adiabatic theory of rotational excitation. On the next Figure (10) I give some of the salient formulae. Unfortunately there is not time to derive any of them here. Historically the basic formula was first derived by Chase²⁸, but in the context of nuclear physics where the problem was the excitation of deformed nuclei. There are two important things to notice about this formula: first that it is not exact but contains an error term is of the order (m/M) ; it is therefore fantastically small for electron-molecule collisions. [One also sees however that for heavier incident particle the theory is probably not particularly good.] Secondly that the dependence of the fixed nuclei on the rotational angle Ω_0 is analytic means that the integral for f can be evaluated analytically. Chase himself did not reduce this integral or the associated cross sections to simplest terms, however, Oksyuk²⁹ who was one of the first to apply this theory seriously to electron-diatomic molecule did work them out in the case in the uncoupled approximation. The phase shifts he used however were derived from a Fisk type calculation⁶, so that although his results are qualitatively impressive, they cannot be taken as quantitatively fundamental. Mittleman, Peacher and Rozsnyai³⁰ applied Chase's theory to rotational excitation of polar (i.e. heteronuclear) molecules, but again their

ADIABATIC THEORY OF ROTATIONAL EXCITATION

FUNDAMENTAL FORMULA

$$f_{\Gamma' \Gamma}(\Omega') = \int d\Omega_0 Y_{\Gamma'}^*(\Omega_0) f(\Omega_0, \Omega') Y_{\Gamma}(\Omega_0) + O\left(\frac{m}{M}\right)$$

CHASE, P.R. 104, 838 (1956)
OKSYUK, JEJP 22, 873 (1966)
MITTLEMAN et al. P.R. 176, 180 (1968)
CHANG & TEMKIN, PRL 23, 399 (1969)
CHANG & TEMKIN, JPSJ (to be published)
HARA, JPSJ 27 1592 (1969)

$$f(\Omega_0, \Omega) = \sum_{m' m} a_{\lambda i} \lambda_{j m} \mathcal{D}_{m' m}^{(\lambda i)}(\beta_0) Y_{\lambda i m'}(\Omega') ; a_0, \beta_0 \equiv \Omega_0$$

$$\sigma' j j = \frac{k_j'}{k_j} \sum_{\lambda \mu} \frac{(\lambda \lambda m \mu)}{2\lambda + 1} \sum_{\lambda \mu} (-1)^{m+\mu} (\lambda \lambda m - m | j_0) (\lambda \lambda \mu - \mu | j_0) (j j_0 | j' 0)^2$$

MEANING OF FIXED-NUCLEI APPROX.

$$Q = \sum_j \sigma' j j = \sum_{\lambda, \gamma, m} \frac{|a_{\lambda m}|^2}{2\lambda + 1} \xrightarrow{\text{UNCOUPLD APPROX.}} \frac{4\pi}{k^2} \sum_{\lambda, m} \sin^2 \gamma_{\lambda m}$$

Figure 10: Rotational excitation of Σ electronic states. Cf. footnote p. 23.

calculation did not utilize scattering parameters of a detailed fixed-nuclei calculation, but used rather a soluble model due to Mittleman and von Holdt³¹. The adiabatic cross sections in the full coupled form for homonuclear case were worked out for neutrals by Chang and myself³² and for charged targets (molecular ions) in an article to be published in the Journal of the Physical Society of Japan³³. Independently Hara³⁴ has derived formulae and applied the adiabatic theory³⁴ to his spheroidal calculation of e-H₂ scattering.

I would like to call three features to your attention. First if we have a rotational transition ($j \neq j'$) then you can see from the final Clebsch-Gordan (C. G.) coefficient that $J \neq 0$; but if $J \neq 0$ then from the first two C. G. coefficients you cannot have both $\ell = \lambda = 0$ i.e. pure s-wave parameters do not contribute to rotational excitation. Since exchange effects are most important in s-waves, I think this explains why such a crude model as the Stier-Fisk model when used in the adiabatic formalism²⁹ can still yield reasonable rotational cross sections.

Not so obvious from $\sigma_{j'j}$ is the fact $\sigma_{j'j} = 0$ for $\Delta j = |j' - j| = \text{odd integer}$.* This comes from the fact that for homonuclear target $a_{\ell\lambda m} = a_{\ell\lambda -m}$ so that the adiabatic theory yields the $\Delta j = \text{even}$ selection rule very simply. Finally if you sum over all final states j' you arrive at an expression which is not only independent of j , the initial state of rotation, but is identical to the fixed-nuclei expression for elastic scattering averaged over classical directions of the internuclear axis¹⁹. It is in this way, then, that one finally learns precisely what it is that

*This only holds if the electronic state is a Σ state. For arbitrary states the results are given by Temkin, Faisal, and Chang (submitted to the Physical Review).

one calculates as elastic scattering in the fixed nuclei approximation: it is the sum over all rotational states starting from any initial rotational state.

A word is in order concerning the threshold behavior and the adiabatic theory. Strictly speaking the error term in Figure 10 is also energy dependent. The error can be minimized by applying the adiabatic theory in an intelligent variation³³, but there appears to be no way of avoiding it altogether. The correct way of accounting for threshold is via the theory of Gerjuoy and Stein³⁵. In our discussion of this problem³³, we have concluded that when the impacting energy exceeds approximately twice the rotational energy difference:

$$k_j^2 \geq 2 \Delta E_{j' j},$$

the adiabatic theory should become valid. This is considerably lower than previous estimates^{29,34}. The Gerjuoy-Stein cross section, which is directly proportional to the quadrupole moment, beautifully accounts for the threshold behavior of the σ_{2-0} rotational excitation³⁶, and in fact can be said to give an experimental verification of the quadrupole moment $Q = 0.48 \pm 0.01 \text{ ea}_0^2$ as Chang has recently shown³⁷. By 0.2 eV above threshold however the Gerjuoy-Stein is low by about a factor of 2 and the enhanced $\Sigma\mu$ (i.e. $m = 0$, p-wave) phase shift will already be entering via the adiabatic theory to account for the experimentally observed augmentation.

The threshold behavior for charged molecular targets (H_2^+) presents an interesting contrast to the foregoing. In an average sense the adiabatic theory

can there be applied down to threshold³³. In fact most of the results can be obtained from the Coulomb Born approximation³⁸. On the other hand this is a case where rotational close coupling would definitely predict series of resonances on top of the adiabatic-background. This comes from the strong coupling of the different rotational states in the presence of the electronic effects on the long range Coulomb tail. Fortunately with the use of a coupled channel quantum defect formalism these resonances can conveniently be parametrized in terms quantum defects of the lower $np\pi$ and $np\sigma$ orbital of the compound system (H_2), their corresponding dipole moments, and the rotational energy constant of the target (H_2^+)³⁹. The significant point is the behavior of the electron in the field of the H_2^+ , wherein it is alternately repelled from the lower rotational state and attracted to the upper rotational, so that the lifetime in the vicinity of the target at a discrete set of energies is long and not short. Thus it violates fundamentally the assumption of the adiabatic theory, which therefore no longer applies, and a discrete set of resonances ensue. What we learn from this is that the semi-classical argument that the electron velocity be large compared to the nuclei is not a guarantee that this is so. Thus the adequacy of the adiabatic theory, as well as the fixed-nuclei approximation for that matter, is partially an a posteriori circumstance.

In the next Figure (11) we give some differential rotational excitation results of H_2 which as shown on the left are dominated by p-waves. Indeed it is the difference between the different m-components which is important, a fact

DIFFERENTIAL ROTATIONAL EXCITATION CROSS SECTION

ADIABATIC THEORY

$$\frac{d\sigma_{j'j}}{d\Omega'} \approx \frac{(j200 \ j'0)^2}{k^2} \left[C_1 \left\{ P_0(\cos\theta') + \frac{1}{5} P_2(\cos\theta') \right\} + C_2 \left\{ P_1 + \frac{3}{7} P_3 \right\} \right]$$

WHERE

$$C_1 \approx \frac{2}{3} \sin^2(\eta_{10} - \eta_{11})$$

$$C_2 \approx \frac{4}{5} \sin(\eta_{10} - \eta_{11}) \sin(\eta_{20} + \eta_{21} - 2\eta_{22}) \cos(\eta_{10} + \eta_{11} - \frac{2}{3} \sum_m \eta_{2m})$$

ROTATIONAL CLOSE COUPLING

$$\frac{d\sigma}{d\Omega'} = \sum A_\lambda(j' \leftarrow j) P_\lambda(\cos\theta')$$

WHERE

$$A_\lambda(j' \leftarrow j) \propto \sum_{j_1 j_2} \sum_{j'_1 j'_2} W(j_1 j_1 j_2 j_2; j \lambda) W(j'_1 j'_1 j'_2 j'_2; j' \lambda) T^{j_1}(j' j'_1; j j_1)^* T^{j_2}(j j_2; j' j'_2)$$

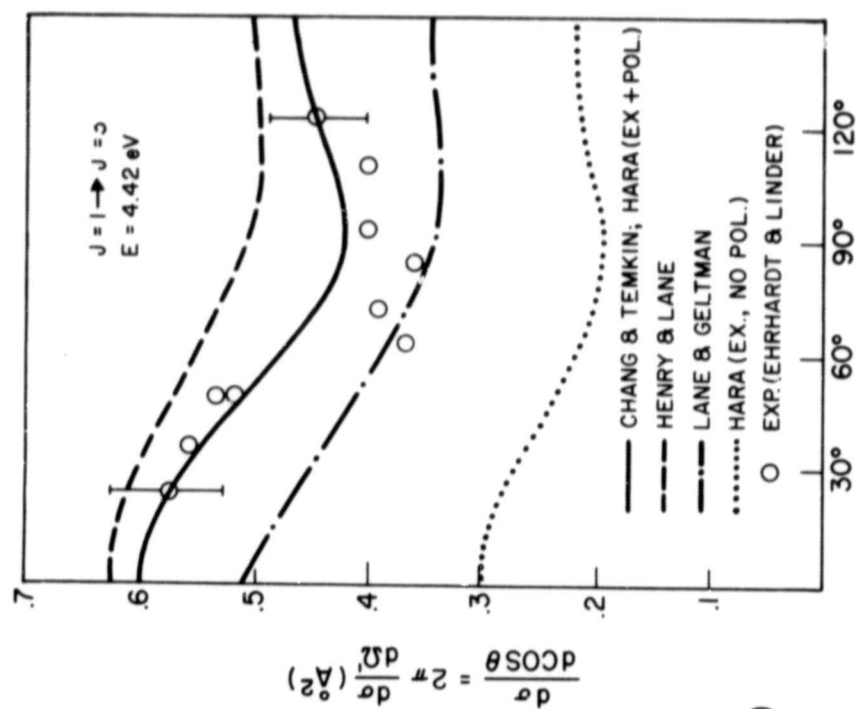


Figure 11

which can readily be appreciated, since it is a non-spherically symmetric effect that is causing the m -dependence and that is also what is applying the torque to the nuclei. The d -wave on the other hand is what causes the asymmetry about 90° and therefore we expect it to be small. Our own calculation³² was performed by fitting the total $\sigma_j \rightarrow j$ cross sections to those Ehrhardt and Linder⁴⁰ and the very accurate swarm results of Crompton, Gibson, and McIntosh³⁶ at even lower energies. Of particular interest is the fact that our results at these energies are indistinguishable from Hara's³⁴, which is another indication of the quality of his results²⁶. The lowest curve is what Hara gets when he does not include polarization. The discrepancy is in line with the close coupling results of Lane et. al.³⁻⁵ when they did not include both exchange and polarization. To give you an idea of the complexity of that calculation, however, I have inserted some close coupling formulae at the bottom! Those authors also noted that the sum over all rotational states (including the elastic) from any given initial state j is independent of j to a high degree of approximation. As we have seen from Figure 10, this result is a necessary consequence of the adiabatic theory.

For all these reasons it is to be expected that the adiabatic and rotational close coupling theories must be accurately related to each other by a unitary transformation. This transformation has been studied recently by Bottcher⁴¹ and Burke and SinFaiLam⁴².

Returning to the adiabatic theory, I present in Figure 12 some $e-H_2^+$ differential cross sections³³. Of particular note is the opposite asymmetry of singlet and triplet results about 90° . This is traceable to the enhancement of the $^3P_{m=0}$ phase shift of which there is no counterpart in the $^1P_{m=0}$ partial wave. This then is an experimental manifestation of the $\Sigma\mu$ enhancement which was such a prominent feature of the $e-H_2$ results.

In summary then I think we can say that calculational understanding of electron-molecule scattering has progressed significantly in the last couple of years. The fixed-nuclei theory provides a reliable and convenient method of calculating the average cross section and coupled with the adiabatic theory, it effectively supersedes rotational close coupling as a method for calculating most aspects of rotational excitation, in my opinion. Single-center expressions, on the other hand, are not on such reliable ground. There is no question that they provide an approximately quantitative description, however, particularly for heavier diatomics the degree of accuracy to which they are practically capable is open to question. To convince you of that I show you on the last Figure (13) a recent very elaborate single-center calculation of $e-N_2$ scattering by Burke and SinFaiLam⁴². In the first place several terms were required both in the partial wave expansion of the scattered wave as well as the spherical expansion of the potential in order to obtain apparent convergence. The agreement with experiment⁴³ as you see is only qualitative. The $^2\Pi_g$ enhancement or shape resonance does not show up gratifyingly in the calculation, but its

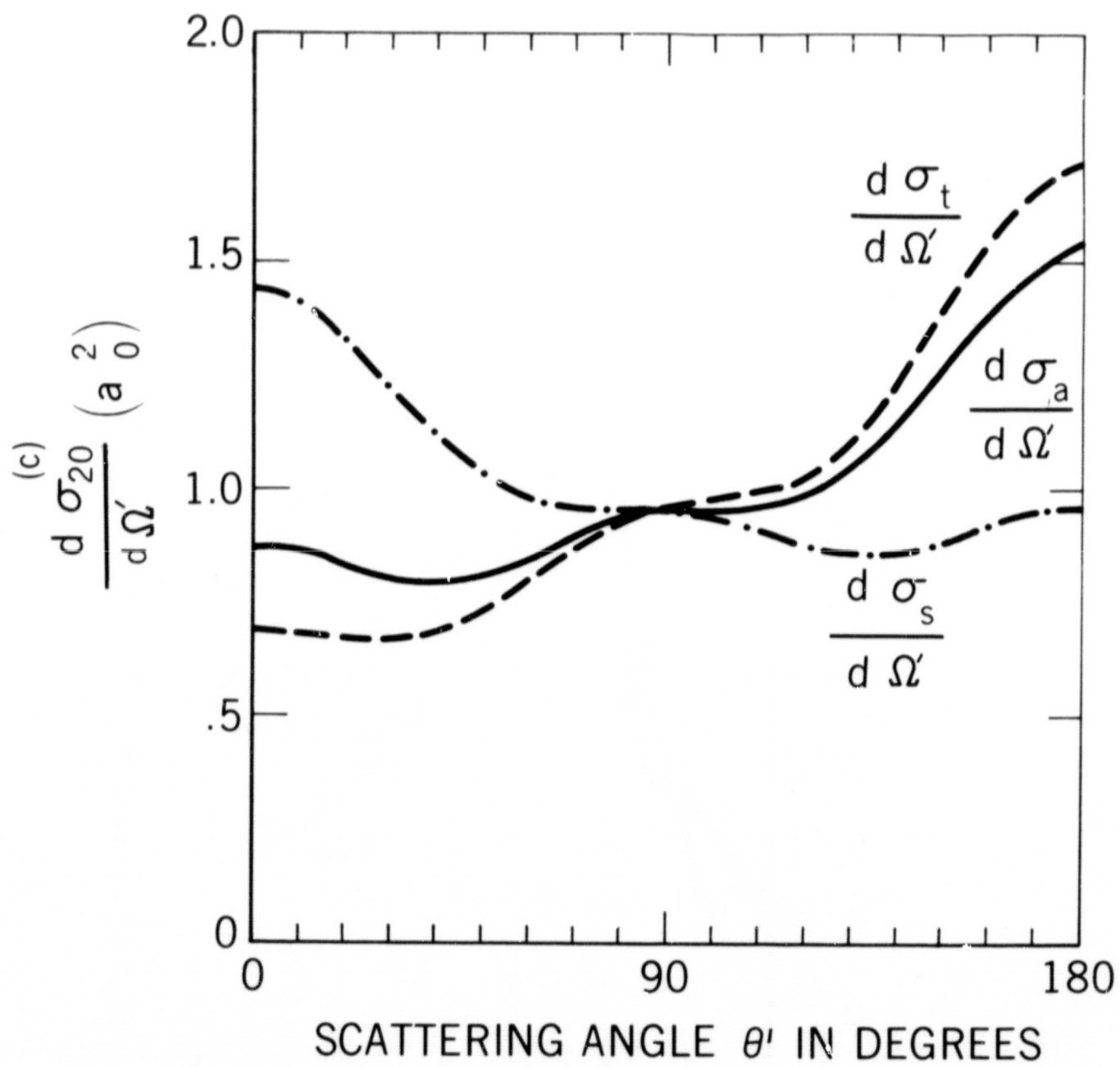


Figure 12

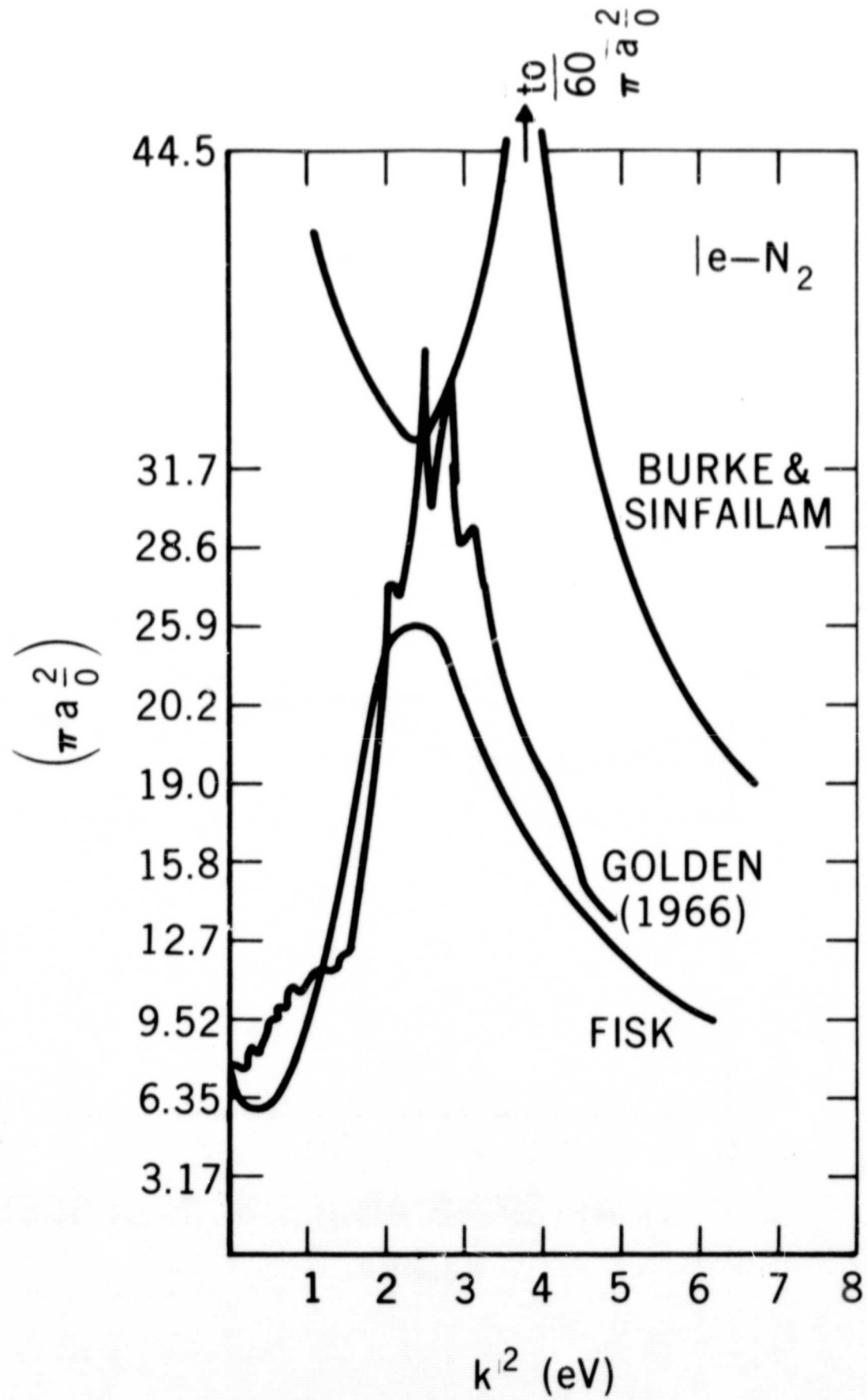


Figure 13

position and height are not really correct. It is possible that part of this is due to incomplete inclusion of polarization in addition to the single-center expansion, but for all the work entailed, one might have hoped for more. Incidentally the lower curve is one calculated by Fisk⁶ 35 years ago. It appears then that spheroidal coordinates will be a necessary part of accurate fixed-nuclei calculations.

The resonances in the experimental curve around 3 eV were first seen by Schulz⁴⁴. They are obviously strongly connected with vibrational structure. The accurate inclusion of the vibrational degrees of freedom present at the present time the most challenging problem in the theory of electron-molecule scattering⁴⁵.

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